Electrochemical Study of Iodide in the Presence of 2-Thiobarbituric Acid- Catalytic Determination of 2-Thiobarbituric Acid☆

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ABSTRACT: *Electrochemical oxidation of iodide has been studied in the presence of 2-thiobarbituric acid using cyclic voltammetry and controlled-potential coulometry. The results indicate that, the resulting iodine takes part in halogenation reaction with 2-thiobarbituric acid. In addition, the present data are indicative of the suitability of iodide as a quasi mediator for determination of 2-thiobarbituric acid in aqueous solutions. The reaction mechanism has been investigated and shown that, the quasi-catalytic peak currents are linearity dependent on the 2-thiobarbituric acid concentration. The method allows the determination of 2-thiobarbituric acid in range 4.0×10^{-5}- 1.0×10^{-3} mol/L. The relative standard deviation for 10 determinations of 1.0×10^{-4} mol/L 2-thiobarbituric acid is 2.2% and the detection limit of the method is 3.9×10^{-5} mol/L.*

KEY WORDS: *Electrochemical oxidation, 2-Thiobarbituric acid, Cyclic voltammetry, Catalytic determination*

INTRODUCTION

As part of our investigations on the mechanistic studies [1-8], we focused our attention on anodic oxidation of iodide in the presence of 2-thiobarbituric acid. This compound (4,6- dihydroxy-2- mercapto-pyrimidine) is used in preparation of thiobarbitals and in chemical analysis for spectrophotometric determination of copper [9,10], iron [10,11], bismuth [12,13] and ruthenium [14] as well as many organic compounds including aldehydes and carbohydrates. It has also been identified as intermediate in many processes. Quantitative determination of 2-thiobarbituric acid is, therefore, very important in studying both the biological and industrial processes. The said compound has been determined previously by titration methods, using silver(I) [15,16] and mercury(II) [17] ions, iodine and iodine-azide [18-24], bromine chloride [25], dichromate ions [26,27], sodium tetraphenylborate [28] and sodium methylate [29]. Spectrophotometric [30-39], polarographic [40-41], cathodic inversion voltamperometry [42], fluorimtric [43,44], capillary electrophoresis [45] and chromatographic methods [46-48] have also been proposed. Unfortunately, 2-thiobarbituric acid with a large overpotential for oxidation at solid electrodes is not suitable for voltammetric methods. In addition, until now, no report has been published on electrocatalytic behavior of 2-thiobarbituric acid. We were prompted to study the electrochemical oxidation of iodide in the

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presence of 2-thiobarbituric acid and propose a mechanism for the electrooxidation of iodide in its presence. In this work we investigate the suitability of a quasi-catalytic method for the determination of 2-thiobarbituric acid. As it turned out the method is a very simple and sensitive procedure for the analysis for 2-thiobarbituric acid.

EXPERIMENTAL

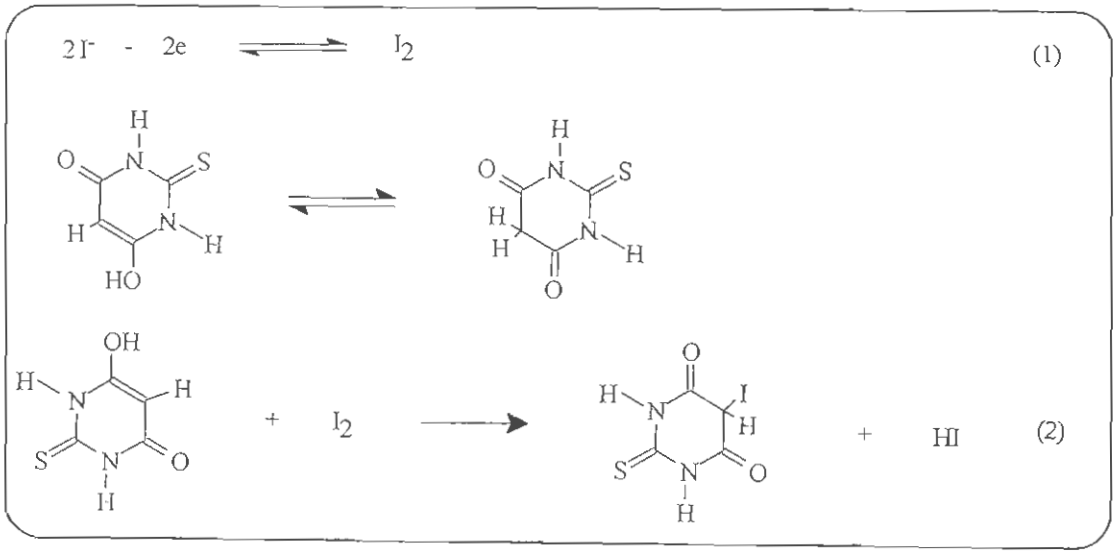
Cyclic voltammetry and controlled-potential coulometry were performed using an Autolab model PGSTA-T20 potentiostat/galvanostat. The working electrode used in the voltammetric experiments was a glassy carbon disc (2 mm diameter) and a platinum wire was used as counter electrode. The working electrode potentials were measured versus the SCE (all electrodes from AZAR electrode, Uromieh, Iran). Reagent-grade 2-thiobarbituric acid (from Aldrich Milwaukee, WI, USA) was used without further purification. The sodium iodide was proanalysis grade (from E.Merck Darmstadt,Germany) and used as received.

RESULTS AND DISCUSSION

Electrochemical study

Cyclic voltammogram of 1×10^{-3} mol/L of sodium iodide in aqueous solution containing 0.1 mol/L hydrochloric acid at 25 °C shows one anodic and a corresponding cathodic peak at 0.49 V and 0.43 V, respectively, which correspons to the transformation of iodide to iodine and vice versa via a two-electron process (Fig. 1, curve a) (Scheme 1, Eq. 1). Fig. 1, curve b, shows the cyclic voltammogram obtained for 1×10^{-3} mol/L solution of iodide in the presence of 1×10^{-3} mol/L 2-thiobarbituric acid. The voltammogram exhibits an increase in anodic current and the disappearance of the cathodic counterpart of the anodic peak. Under these conditions proportional to the increase of sweep rate, the cathodic peak appears and the height of which increases progressively with scan rate (Fig. 2). Moreover, a plot of the peak current ratio (I_{pc} / I_{pa}) as a function of scan rate (Fig. 2, inset) is in good agreement with the occurrence of a chemical reaction after the electron transfer [49]. The multi-cyclic voltammetry of iodide in the presence of 2-thiobarbituric acid shows that the shift of peak A in a positive direction. This shift in the presence of 2-thiobarbituric acid is due to product deposition an the electrode surface, inhibiting to a certain extent the performance of the electrode process [1-8]. In addition controlled-potential coulometry was performed in solution containing 5×10^{-3} mol/L sodium iodide and 5×10^{-3} mol/L of 2-thiobarbituric acid at 0.6 V vs. The SCE, the monitoring of the electrolysis progress by cyclic voltammetry shows that as the electrolysis proceeds, the anodic peak decreases and finally disappears.

We assume that such a behavior is an indication of a chemical reaction between iodine and 2-thiobarbituric acid according to the Scheme (1).



Scheme (1)

Such a mechanism is also in good agreement with the results already proposed about electrochemical halogenation of dibenzoylmethane [50], dimedone [51] and barbituric acid [52]. The interesting feature of this mechanism, is its similarity to the EC mechanism (following reaction), with respect to the iodine reaction with 2-thiobarbituric acid. On the other hand, regeneration of iodide ion on the electrode surface indicates its resemblance to the EC' mechanism(catalytic reaction). Based on this mechanism, the increase in I_{pa} in the presence of 2-thiobarbituric acid (Fig. 1, curve b) is related to the regeneration of iodide at the surface of electrode [49] (Scheme 1, Eq. 2).

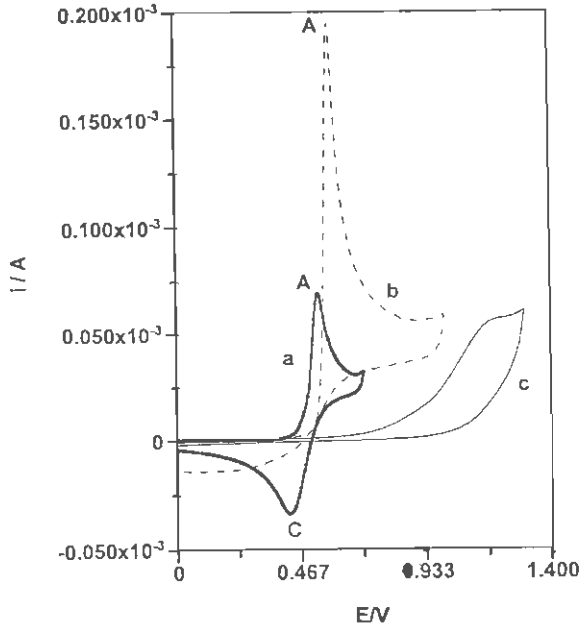


Fig.1: Cyclic voltammograms of 1×10^{-3} mol/L sodium iodide: (a) in the absence, (b) in the presence of 1×10^{-3} mol/L 2-thiobarbituric acid and (c) 1×10^{-3} mol/L 2-thiobarbituric acid, at GC electrode in aqueous solution containing 0.1 mol/L hydrochloric acid. Scan rate: 50 mV s^{-1}, T = 25 ± 1 °C

Analytical aspects

Optimization of the solution pH

According to Scheme (1), the anodic peak current (I_{pa}) of iodide in the presence of 2-thiobarbituric acid is a quasi-catalytic current that depends on the concentration of 2-thiobarbituric acid and the solution pH. Therefore the effect of the pH was studied in the range of 1 to 10 (Fig. 3). In this figure I_p^{cat} is the anodic peak current of iodide in the presence of 2-thiobarbituric acid and I_p^d is the anodic peak current of iodide in the absence of 2-thiobarbituric acid. As shown in this figure, the solution pH clearly affects the current peak ratio (I_p^{cat} / I_p^d).

In accordance with these findings all experimental measurements were performed in 0.1 mol/L hydrochloric acid.

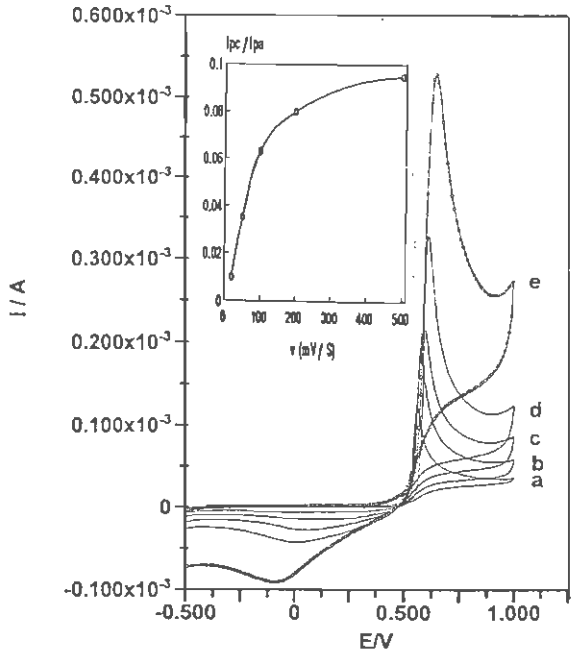


Fig.2: Cyclic voltammograms of 1×10^{-3} mol/L sodium iodide in the presence of 1×10^{-3} mol/L 2-thiobarbituric acid at GC electrode, at various scan rates. Scan rates from (a) to (e) are: 20,50, 100, 200 and 500 mV s^{-1}, respectively. T=25±1 °C. Inset: variation of peak current ratio (I_{pc}/I_{pa}) as a function of the scan rate

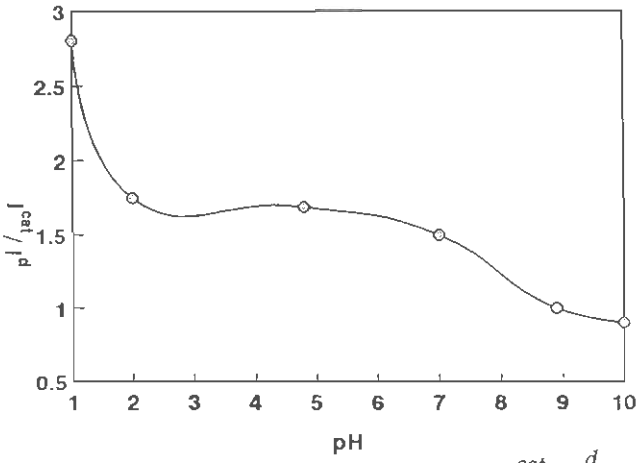


Fig. 3: Effects of pH on the peak current ratio (I_p^{cat} / I_p^d).

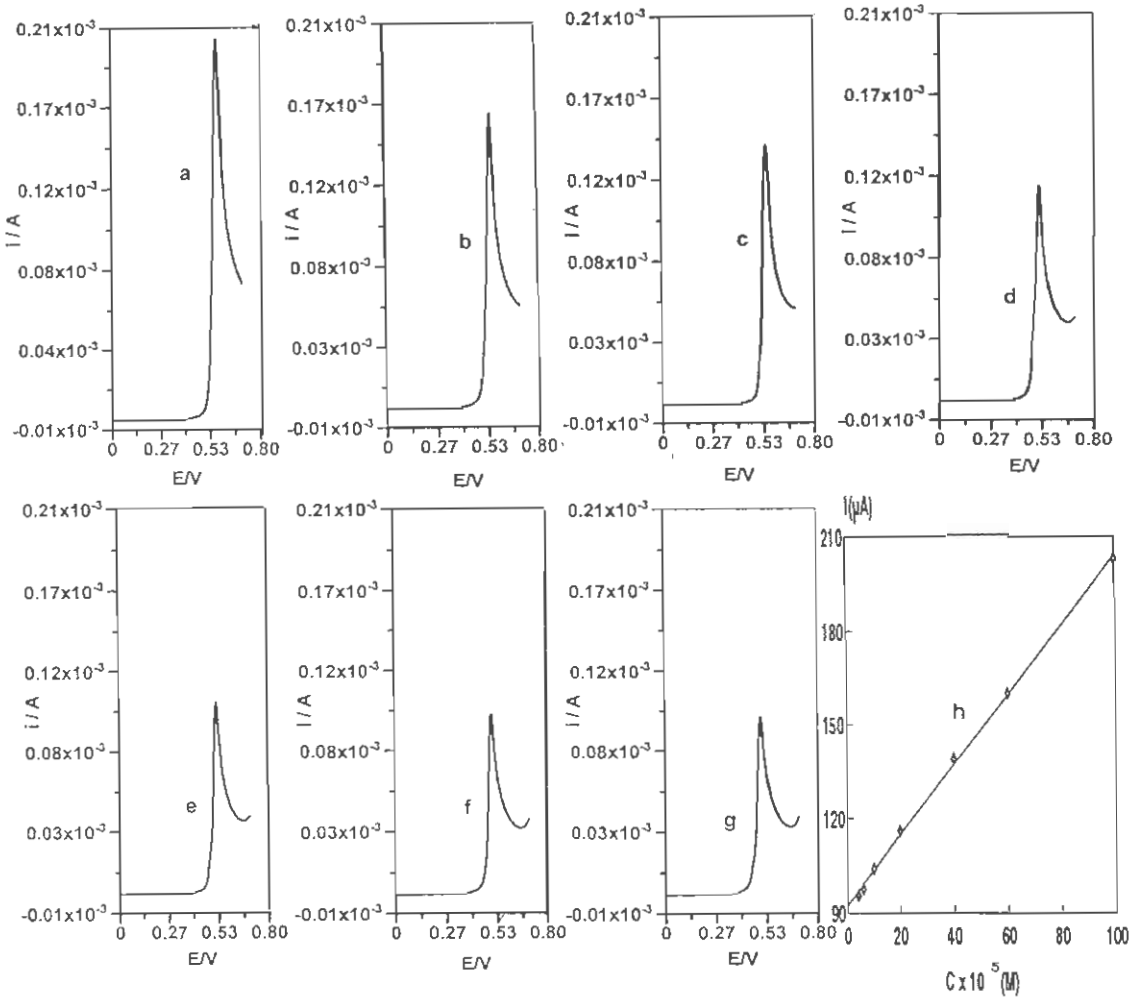


Fig. 4: Linear sweep voltammograms of 1×10^{-3} mol/L sodium iodide at various amounts of 2-thiobarbituric acid concentration. 2-Thiobarbituric acid concentrations from (a) to (g) are: 1.0×10^{-3}, 6.0×10^{-4}, 4.0×10^{-4}, 2.0×10^{-4}, 1.0×10^{-4}, 6.0×10^{-5} and 4.0×10^{-5} mol/L. Scan rate: 50 mV s^{-1}. (h) Calib-ration curve for the determination of 2-thiobarbituric acid in the presence of iodide

Optimization of the scan rate

The influence of scan rate, v, on the anodic peak current of iodide in the presence and absence of 2-thiobarbituric acid was examined in the range of 10-500 mVs^{-1}. The maximal ratio of I_p^{cat} / I_p^{d} was obtained at v = 50 mVs^{-1} which was used throughout this work.

Determination of 2-thiobarbituric acid

Linear sweep voltammetry (LSV) of iodide at a glassy carbon electrode, in the presence of 2-thiobarbituric acid showed that quasi-catalytic peak of iodide was linearly dependent on the concentration of 2-thiobarbituric acid. The calibration curve obtained under the optimum conditions for a solution containing 1.0×10^{-3} mol/L of sodium iodide, is linear in the range of 4.0×10^{-5}-1.0×10^{-3} mol/L with a correlation coefficient of 0.999 (Fig. 4). The regression linear equation is $y = 9.24\times10^{-5} + 1.12\times10^{-1}x$, where x= concentration of 2-thiobarbi-turic acid, and y=peak current. The detection limit, of 2-thiobarbituric acid defined as $C_l = 3S_B/m$, where C_l is limit of detection, S_B is the standard deviation of the blank signal and m is the slop of calibration graph was 3.9×10^{-5} mol/L.

To evaluate the relative standard deviation of the method a series of independent standard samples was used. The results are given in Table 1.

Table 1: Relative standard deviation of the proposed method

2-Thiobarbituric acid concentration (mol/L)	R.S.D (%) (n=10)
4.0×10^{-5}	2.6
1.0×10^{-4}	2.2
4.0×10^{-4}	1.9
1.0×10^{-3}	1.7

Interference Study

In order to assess the possible analytical application of the quasi catalytic method described above; the effect of some probable interfering organic and inorganic substances was tested. It was found that many organic compounds (except β-diketones and β–ketoesters) such as formaldehyde, acetaldehyde, acetone, ethanol, methanol, 2-propanol, 1,2,3-propantriol, ethylenglycol, ethylenediamine and inorganic ions such as: Mg^{2+}, Ca^{2+}, Al^{3+}, Ba^{2+}, Zn^{2+}, Ni^{2+}, Fe^{2+}, Cd^{2+} and Co^{2+} do not interfere even at high concentrations.

CONCLUSIONS

The results of this work show that iodide can act as a mediator in the determination of 2-thiobarbituric acid. The reaction mechanism for anodic oxidation of iodide in the presence of 2-thiobarbituric acid is presented in Scheme 1. The approach presented provides a new facile method for determination of 2-thiobarbituric acid concentration that can be used for determination of other β-diketones and β-ketoesters..

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